STUDIES ON MULTIFUNCTIONAL PROPERTIES OF MULTIFERROIC NANOCOMPOSITES

Introduction

Multiferroic materials that are simultaneously ferromagnetic and ferroelectric in the same phase have attracted great attention of the researchers worldwide. The possibility of modulating electrical polarization with a magnetic field and magnetization with an electric field (known as magnetoelectric (ME) effect) in these materials, making them highly prized for spintronic and other magnetoelectric applications. Multiferroics originally refers to the coexistence of both ferromagnetic and ferroelectric orders [1]. However by this strict definition, multiferroics would be rarely realized in a single-phase material. Nowadays the scope of multiferroics has been extended to include any case in which spontaneous magnetic and dielectric orders coexist. The attractive feature of these materials is not so much the value of the electrical polarization, which is several orders of magnitude smaller than for typical ferroelectrics but rather the very large cross-coupling between magnetic and electric properties, which makes the 'novel' multiferroics enticing paradigms of functional behavior [2]. Multiferroic magnetoelectrics maintain a magnetization and dielectric polarization which can be modulated and activated by an electric field and magnetic field respectively. For this reason, multiferroic materials are being considered for a host of potential applications as diverse as additives, magnetic recording media, information storage, spintronics and sensors [3-5].

In multiferroic materials, researchers may expect a strong cross coupling between ferroelectricity and magnetism that provides additional freedom for magnetization and polarization manipulation that is the control of polarization by a magnetic field and of magnetization by an electric field. Therefore, the field of multiferroics and ME effects has attracted research focus because of their great potential for technological applications as well as the intriguing fundamental physics. Magnetoelectric materials which show ME coupling have been in existence since 1960's and was first demonstrated in an unoriented Cr_2O_3 crystal by Astrov [6]. However, there are very few naturally or synthetic multiferroic materials that exhibit ferromagnetism and ferroelectricity in a single phase. The first discovered multiferroic material was nickel iodine boracites ($Ni_3B_2O_{13}I$, Rochelle salt) and

after which the series of multiferroic boracites compounds having complex structure with atoms per formula unit and more than one formula unit per unit cell have been synthesized[7-8]. After that the research for other ferromagnetic and ferroelectric materials started extensively. In the past, several compounds have been discovered for its magnetoelectric effect which profound the highly fascinating multiferroic research. However, in single phase compounds the magnetoelectric effect is usually too weak to be practically applicable.

One way to substantially improve the coupling between electric and magnetic orders is to utilize strong internal electromagnetic fields in the materials with large magnetic and electric susceptibilities. It is well known that the largest magnetic/electric susceptibilities are found in ferromagnetic/ ferroelectric materials, respectively. Ferroelectrics with ferromagnetism, i.e. ferroelectromagnets could be utilized for an improved magneto – electric effect [9]. However, it has proved difficult to discover new intrinsic multiferroic materials because the mechanisms driving ferroelectricity and ferromagnetism simultaneously are generally incompatible. Ferroelectricity is usually driven by transition metal compounds with empty d – orbits (d^0). On the other hand, ferromagnetism usually requires a transition metal with partially filled d – orbitals. Consequently, a different approach is required to combine these two properties.

Multiferroic nanocomposites with considerable design made by incorporating ferroelectric (FE) and ferromagnetic (FM) substances have spawned remarkable attention in earlier years due to its multifunctional properties. The coupling interplay between FE and FM orders at room temperature would generate a substantial ME effect in the composite than in the single-phase material. The Magnetoelectric effect is a product property suggested by van Suchtelen in the year 1972[6]. The phase connectivity and interfacial bonding of the ferroelectric and ferromagnetic phases have a strong impact on mechanical coupling in the composites. Currently, many research groups and industries are performing extensive research on composite nanostructures to gain large magnetoelectric coupling coefficient for possible device applications, which includes sensors, magnetoelectric transducers and actuators, magnetic recording media, and so on [10-11].

Amongst all single phase multiferroics, $BiFeO_3$ (BFO) is an extensively investigated material worldwide. The $BiFeO_3$-based multiferroics are interesting materials for basic research as well as for possible application in magnetoelectric devices. For large magnetoelectric coupling, ferroelectricity and spontaneous magnetization should coexist

within the same structural phase. In the bulk form, it is an antiferromagnetic, ferroelectric and ferroelastic multiferroic material with electric, magnetic and structural ordering temperatures well above room temperature. The coexistence of spontaneous magnetization and electric polarization has been reported in nano sized $BiFeO_3$. For single phase material BFO possess significant challenges e.g., formation of impurity phases during synthesis, low magnetization, weak magnetoelectric coupling, and high leakage current caused by volatile nature of Bi ions and due to formation of oxygen vacancies[12]. Both its spontaneous polarization and saturation magnetization are disappointingly low as compared to many standard ferroelectrics and ferromagnets. This is due to the superimposition of a spiral spin structure on BFO antiferromagnetic order. In this spiral spin structure, the antiferromagnetic axis rotate through the crystal with an incommensurate long wavelength period of 62 nm[3], which cancels the macroscopic magnetization and also inhibits the observation of the linear magnetoelectric effect in bulk $BiFeO_3$. Hence for novel electronic applications of BFO, its magnetic and electronic properties must be enhanced. It is widely expected that the strategies based on nanotechnology and aliovalent ion doping will have a great impact on their magnetic, electrical and magnetoelectric properties as a result of the suppression of the helical order and quantum confinement effect [13].

Researchers have done many investigations competently to attain improved multiferroic properties with optimal ME coupling coefficient in BFO for multifunctional device applications by substituting various transition metals, alkaline earth metals, lanthanides on A-site and B-site cation of BFO or by producing nanocomposites of BFO [14 -18]. In the recent decades, it is noted that $BiFeO_3$ based nanocomposites combined with perovskite oxides and ferrite spinels fabricated desirable greater ME response than single phase compound. Out of the several nanocomposites, ferrite oxide composites hold good electric and magnetic properties besides their cross-coupling between ferroicities. In such compounds, spontaneous polarization could be directed by an external magnetic field and vice versa. Indeed, spinel ferrites are excellent magnetic counterparts in the formation of multiferroic nanocomposites because of their low electrical conductivity, dynamic orbital coupling, low dielectric constant, high magnetic loss, good mechanical hardness, fine chemical stability, high surface area[19 - 20]. It plays a significant role for ME applications by applying piezomagnetic and piezoelectric effects near room temperature. The ME coupling voltage produced across the composites is associated with transferring stress from the magnetostrictive phase to the ferroelectric phase in the material under an external

magnetic field which generates electrical polarization via the ME effect. Hence the incorporation of spinel ferrites like $NiFe_2O_4$ and $MnFe_2O_4$ in BFO matrix, are expected to enhance the magnetic, dielectric, magnetoelectric as well as ferroelectric properties of the composite.

Rare earth element substitution is found to be an efficient way to solve the issue of severe current leakage due to the defects and non-stoichiometry. The incorporation of materials with high leakage into practical devices is very challenging. Hence solving the leakage problem is a necessary step. It has been reported that doping of small amount of La atoms improved the leakage current characteristic and the magnetic properties of BFO [21 - 23]. Hence, the influence of La doping along with the BFO composites and their structural, magnetic, electric, and magnetoelectric properties have been investigated.

It has been observed from the reports that Gamma radiation exposure is also an emerging as an excellent novel method for control of sample properties. Indeed this could be an a unique and essential tool for altering sample properties both structural, physical, chemical, electrical, magnetic and magnetoelectric [24 -27] not only for the purpose of producing fine quality samples but this would also address the much required issue of understanding the behavior of electronics in the high energy radiation environment. Gamma (γ rays) radiation with high energy (1.17MeV to 1.33MeV) interacts with an electronic shell or the atomic nuclei of the substance when exposed. These interactions results in an elastic and inelastic scattering of the particles causing excitation and ionization of the atoms, initiation of nuclear reactions and also disturbance in the structure of the matter, termed as radiation damage. The studies of the modification in multiferroic material due to irradiation are of both technological importance and scientific interest. As multiferroic materials in nano as well as bulk form are extensively in use in various fields including in areas of gamma radiation abundance like nuclear reactors, satellites in outer space, satellite launch vehicles and medical applications, it becomes important study to know the response of multiferroic nanomaterial to gamma radiation with respect to the affected properties [28 - 29].

Polymer host multiferroic nanocomposites are appropriate for device application because they are highly flexible and can be casted in thin film form. Several other problems such as high leakage current and dielectric loss, which lead to failure during operation can be eliminated in these polymer based composites. In this kind of nanocomposites, the interface effects between nanoparticles and the polymer matrix becomes a prominent factor

in determining their physical properties. Significant improvement in the ME response is observed in polymer based nanocomposite films. In the past several years, a significant amount of work has been carried out on various polymer- ceramic composites. Another approach to obtain a good ME coupling is the development of particulate composites within a polymer matrix which reduces leakage current and loss. PMMA is a very good insulating and ferroelectric polymer. The dielectric constant and dielectric loss of this polymer have been reported to be ∼2.6 and 0.014 respectively at 1 MHz frequency. The low dielectric loss of this polymer enables it to be used as a matrix in nanocomposites [30 -34].

Aim and objectives of the work

The major goal of this research is to synthesize multiferroic nanocomposites with ferroelectric and magnetic characteristics that are coupled. More precisely, we use various synthesis and modification procedures, to improve the magnetic, electric, and magnetoelectric properties of $BiFeO_3$ by mixing it with spinel ferrites.

The specific objectives are:

- To synthesize $BiFeO_3$ - RFe_2O_4 nanocomposites (R = Mn, Ni)
- To synthesize La- doped $BiFeO_3$ - RFe_2O_4 nanocomposites (R = Mn, Ni)
- To study the effect of gamma irradiation on $BiFeO_3$ - RFe_2O_4 nanocomposites (R = Mn, Ni)
- To synthesize PMMA - $BiFeO_3$ - $MnFe_2O_4$ polymer nanocomposites.
- To study the structural and morphological properties of the synthesized nanocomposites.
- To investigate magnetic, electric and magnetoelectric properties of the synthesized nanocomposites.

The present work involves the preparation of $BiFeO_3$ - RFe_2O_4 nanocomposites (R = Mn, Ni) using the Pechini method. A variety of approaches were used to characterize the structural, magnetic, dielectric, and magnetoelectric properties in a systematic manner. The research looked at different synthesis processes for creating composites and determining their physical properties. Doping was used to change the magnetic and electric characteristics of the material. The effects of gamma irradiation on multiferroic characteristics of nanocomposites have been investigated. Developing specific nanocomposites within polymer matrixes to improve multiferroic properties is an intriguing and less explored approach. Solvent casting is used in the present study to fabricate

multiferroic nanocomposites based on PMMA. The crystalline structure, morphology, and other features have all been well studied. Multiferroic nanocomposites comprising ferroelectric and magnetic phases often give a good ME coupling response at room temperature, making them appropriate for advanced technological applications as compared to single phase multiferroic compounds.

Organization of the thesis

The thesis entitled **"Studies on multifunctional properties of multiferroic nanocomposites."** is divided into 7 chapters and the contents of each chapter is briefly explained below.

Chapter 1: Introduction

This chapter would give a general introduction to nanomaterials, multiferroics, single-phase multiferroic materials, and multiferroic composites. It also details the multiferroic nanostructures and the differences between their bulk and nano characteristics. The advantages of the composite nanomaterial over single-phase compounds are also highlighted. The background and motivation of the study have been discussed, along with a detailed review of previous work on multiferroic nanocomposites. It also contains the scope of the present research work, which includes the spinel ferrites and their importance as composite partners for composite preparation, rare earth element doping advantages, gamma irradiation study, and polymer nanocomposites are outlined briefly. Finally, the aim and objectives of the work are presented along with the thesis structure.

Chapter 2: Experimental Procedures and Characterization Techniques

This chapter goes over the procedures for the synthesis and characterization of nanocomposites in detail. The Pechini method was used to make the composites (modified sol-gel method). A greater understanding of the characteristics of the synthesized nanocomposites is required to fully comprehend their potential. Therefore, the crystalline structure, morphological, magnetic, dielectric, ferroelectric, and magnetoelectric properties of produced composites have been studied. X-ray diffraction, scanning electron microscopy, transmission electron microscopy, atomic force microscopy, Fourier infrared microscopy, Impedance analyzer, P-E loop tracer, vibrating sample magnetometer, and lock-in amplifier set-up are among the techniques used to characterize the prepared composites.

Chapter 3: Multiferroic Properties $BiFeO_3$ - RFe_2O_4 (R= Mn, Ni) nanocomposites

This chapter describes the successful synthesis of $BiFeO_3$ - $MnFe_2O_4$ nanocomposites using Pechini method. The structural, electric, magnetic and magnetoelectric properties are discussed. The rhombohedral structured perovskite $BiFeO_3$ (BFO) and spinel cubic phase of $MnFe_2O_4$ (MFO) in the composite is confirmed from the X-ray diffraction pattern. The results of microstructural analysis obtained, using FESEM and HRTEM is an evidence of two distinct phases in the composite, which matched with XRD results. The ordered magnetic structure of $BiFeO_3$ - $MnFe_2O_4$ nanocomposite, in all compositions showed good exchange coupling interaction between two phases. The dielectric behavior of synthesized materials is realized by the interfacial phenomena of ferromagnetic and ferroelectric phases. The Nyquist's plot revealed the occurrence of non Debye relaxation in the composites. Although, the simultaneous existence of magnetic and electric properties is observed in the samples, the volume fraction and resistivity of ferromagnetic material has a great influence on the magnetoelectric coupling coefficient of the studied material. The maximum estimated magnetoelectric coupling coefficient value is found to be $\alpha = 25.39$ mV cm^{-1} Oe^{-1} for 70% $BiFeO_3$ – 30% $MnFe_2O_4$ nanocomposite. (*The results of this work are published in ELSEVIER - Ceramics International, 2021, 47, Pages 15267-15276).*

This chapter also discusses a systematic study of the multiferroic properties of the perovskite (BFO)–spinel (NFO) nanocomposites prepared via the simple Pechini method. The powder X-ray diffraction analysis revealed the presence of individual phases in the composites. Moreover, the crystallite size, lattice constants, cell volume, strain, dislocation density, and surface area are greatly influenced with the incorporation NFO into BFO, thereby enhancing the dielectric, magnetic, and magnetoelectric properties. The FESEM technique evidenced the agglomerated configuration of the grains and its size varied in the range of 38 – 45 nm. The room temperature magnetic hysteresis curve established the ordered good ferromagnetic nature and changes in magnetic saturation (M_s), remanent magnetization (M_r), magnetic anisotropy (K), and magnetic moment (μ) with an increasing NFO concentration. The electrical conductivity and dielectric performance of the composites are strongly affected by the concentration of NFO. An observed asymmetric and depressed semicircle that indicates non-Debye relaxation in the material is revealed through impedance analyses. The obtained unsaturated and lossy P–E loop disclosed the conducting nature of the nanocomposites. The merging of the perovskite/spinel structured phases in the

composite manifests better magnetoelectric performance with improved coupling coefficient (*The results of this work are published in RSC - Nanoscale advances, 2021, 3, 4866).*

Chapter 4: Gamma irradiation induced modifications on multiferroic properties of BiFeO3 - RFe_2O_4 (R= Mn, Ni) nanocomposites.

This chapter unfolds all the results of investigations carried out on gamma-irradiated $BiFeO_3$-$MnFe_2O_4$ and $BiFeO_3$-$NiFe_2O_4$ nanocomposites. The 0.5BiFeO3–0.5RFe2O4 (R = Ni, Mn) nanocomposites have been synthesized using the Pechini method. At a rate of 2.6 kGy/minute, the samples were irradiated with different doses of 60Co-radiation: 500 Gy, 5 kGy, and 25 kGy. The impacts of different doses of high energy gamma irradiation on the structural, electric, magnetic, and magnetoelectric properties of both composites are studied. The effects of irradiation on surface morphology and the existence of a few impurity phases have been studied by scanning electron microscopy and X-ray diffraction. Irradiation has produced changes in the dielectric spectrum in the frequency range between 100 Hz and 2 MHz. Exposure to gamma radiation brings about key changes in the properties as a consequence of a few structural parameters. The results show that dielectric loss and dielectric constant are greatly dependent on radiation dose. There is a slight increase in magnetic saturation and a decrease in coercivity that can be observed in the samples after irradiation in both composites. Irradiated $BiFeO_3$-$MnFe_2O_4$ nanocomposites show better ME behavior and a higher coupling coefficient than unirradiated ones. But the investigations into $BiFeO_3$-$NiFe_2O_4$ nanocomposites revealed the possibility of highly ionizing radiation degrading the dielectric and multiferroic properties. Therefore, the irradiation studies on $BiFeO_3$-$MnFe_2O_4$ and $BiFeO_3$-$NiFe_2O_4$ nanocomposites give an idea about the performance of the magnetoelectric devices near intense radiation sources and in spacecraft.

Chapter 5: The effect of La doping on multiferroic properties of $BiFeO_3$ - RFe_2O_4 (R= Mn, Ni) nanocomposites.

This chapter details the effect La doping on multiferroic properties of the $BiFeO_3$-$MnFe_2O_4$ and $BiFeO_3$- $NiFe_2O_4$ nanocomposites. La doped $0.7Bi_{(1-x)}La_xFeO_3$ - $0.3RFe_2O_4$ nanocomposites (R = Mn, Ni), x = 0, 0.1, 0.2 were synthesized using Pechini method. It is expected that the incorporation of small amount of La reduces the production of impurity

phases, reduce oxygen vacancies, and improves ferroelectric, ferromagnetic and magnetoelectric properties. Therefore the effect of La on the structural, magnetic, dielectric and magnetoelectric properties is studied. Structural analyses were performed using XRD and SEM techniques. Improved dielectric response ferroelectric characteristics have been observed in both composites. Magnetic measurements revealed the enhancement of ferromagnetic property with increasing La doping in the samples. In order to explore the multiferroic properties of La doped samples, their magnetoelectric coupling studies were performed using a lock-in amplifier technique. The magnetoelectric coupling (ME) coefficient (α) of La doped BFO – MFO samples has been reduced, but La doped BFO – NFO sample (x = 0.2) showed high ME coefficient than the undoped sample.

Chapter 6: Structural, magnetic, dielectric and magnetoelectric properties of $BiFeO_3$ - $MnFe_2O_4$ - PMMA films.

Ceramic polymer composites have become potential candidates for integration into high frequency electronics. Polymethyl methacrylate (PMMA) has been chosen as the matrix due to low dielectric loss of the polymer. In this chapter, the fabrication and characterization of $BiFeO_3$ - $MnFe_2O_4$ - PMMA films is detailed. Initially the ceramic particles were prepared by Pechini method. Then PMMA- BiFeO3- $MnFe_2O_4$ films were prepared by solvent casting method. Structural analysis was performed using XRD, SEM and AFM. The presence of both BFO - MFO nanoparticle and PMMA peaks in the XRD pattern of nanocomposite indicated the development of both polymer as well as ceramic phases. The agglomeration of the particles was found to increase with the increase of the loading percentage of BFO - MFO particles. The FTIR spectra confirmed the complexation and interaction among the compounds. Dielectric properties in the frequency range of 40 Hz - 2MHz showed the value of dielectric constant of the polymer nanocomposite was significantly increased with increase in loading percentage of nanoparticles as compared to pure PMMA. It also showed inherent low dielectric loss in a wide range of frequencies. Development of well saturated magnetic hysteresis loop confirmed the retained ferromagnetic nature in the PMMA-BFO- MFO nanocomposites. The magnetoelectric coupling study shows good coupling between the electric and magnetic phase for the composites.

Chapter 7: Summary and future scope

Nanoscale multiferroic structures have received extensive attention in recent years due to their potential applications in various fields as well as fundamental point of view. The ultimate goal of device functionality can be achieved by multiferroic nanocomposites with strong ME coupling between the order parameters. One of the two phases should be piezomagnetic or magnetostrictive while the other should be piezoelectric or electrostrictive. Commonly, ferroelectrics in combination with ferromagnets are used for this purpose. In the present study multiferroic $BiFeO_3$ based nanocomposites are synthesized using spinel ferrites ($MnFe_2O_4$ and $NiFe_2O_4$) is selected as ferromagnetic counterpart. It is synthesized using a very simple and cost-effective method called Pechini method (modified sol-gel method) and characterized for their magnetic, dielectric, ferroelectric and magnetoelectric properties in a systematic way. The significant differences and improved magnetoelectric coupling coefficient could observe in the composites to employ them for device purposes. Enhancement of magnetoelectric coupling properties is proved by doping of rare earth element (La) on these synthesized composites. Exposure to γ-radiation brings about key changes in the magnetic, electric and magnetoelectric properties as a consequence of few structural parameters. The dispersion of $BiFeO_3$ - $MnFe_2O_4$ nanoparticles in PMMA matrix improved dielectric properties with low dielectric loss, but its weak ferromagnetic behavior reduces its magnetoelectric coupling coefficient. The research on $BiFeO_3$ based nanocomposites have opened the doors to some very unique and exciting capabilities in the field of multiferroics for the application of ME devices. In addition, this chapter also has provided the future scope in this field of research.

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[1] **Preethy Augustine**, Y. Narayana, N. Kalarikkal, An effective strategy for the development of multiferroic composite nanostructures with enhanced magnetoelectric coupling performance: a perovskite–spinel approach, ***Nanoscale Adv.*** 3 (2021) 4866–4877. https://doi.org/10.1039/d1na00376c.

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Under communication

[1] Preethy Augustine, Narayana Yerol, Arun K.J, Impact of gamma irradiation on the structural, electrical, magnetic and magnetoelectric coupling behavior of nanostructured $BiFeO_3$ –($MnFe_2O_4$ composite. (***Dalton Transactions, RSC***)

[2] Preethy Augustine, Narayana Yerol, Arun K.J, Gamma irradiation induced modifications on magnetic, electric and magnetoelectric properties of $BiFeO_3$ – $NiFe_2O_4$nanocomposite. **(*Material Research Bulletin, Elsevier***)

[3] Preethy Augustine, Narayana Yerol, Arun K.J, The effect of La doping on multiferroic properties of $BiFeO_3$ - $MnFe_2O_4$ nanocomposites***. (Scripta materialia, Elsevier)***

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[5] Preethy Augustine, Narayana Yerol, Arun K.J, N. Kalarikkal Flexible polymer nanocomposite film of $BiFeO_3$ - $MnFe_2O_4$ – PMMA for magnetoelectric device applications.***(European polymer journal, Elsevier)***

Papers presented in International conferences

1. **Preethy Augustine**, Y. Narayana, N. Kalarikkal, ***'Enhancement of room temperature Magnetoelectric coupling effect in perovskite-spinel nanocomposites.'*** International Conference on Laser Deposition (iCOLD-2019), Alva's Institute of Engineering and Technology, Mijar, Mangalore, November 27 - 29, 2019 .
2. **Preethy Augustine**, Y. Narayana, N. Kalarikkal, ***'Influence of spinel ferrites in the modification of magneto-electric coupling effect in BiFeO3.'*** International Conference on Science and Technology of Advanced Materials (STAM 20), Mar Athanasius college, Kothamangalam, Kerala, January14 - 16, 2020
3. **Preethy Augustine**, Y. Narayana, N. Kalarikkal, ***'$BiFeO_3$ - $MnFe_2O_4$ nanocomposite with multiferroic properties.'*** 2nd International Conference on Sustainable Urban Development Resource conservation and Food Security (SURF 2020), Received **'BEST PAPER AWARD'**, Bearys Knowledge Campus, Near Mangalore university, Mangalore, Karnataka, August 6-8, 2020.
4. **Preethy Augustine**, Y. Narayana, N. Kalarikkal, ***'Effect of $NiFe_2O_4$ on dielectric and magnetoelectric properties of multiferroic $BiFeO_3$ nanocomposite.'*** International Conference on Advanced Materials for Energy and Environmental applications (ICAMEEA 2020), School of Chemistry and Humanities, BIST, BIHER, December 3 - 4, 2020.

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